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Some New Metallocenes

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SOME NEW METALLOCENES

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Born [redacted] in Vine Grove, Kentucky. Attended North Hardin High School from 1962 until 1966. Enrolled in Western Kentucky University in 1966 and graduated with a bachelor of science in 1970. Served four years as a Spanish linguist for the United States Air Force and entered Western Kentucky University in 1974 to obtain a master of science degree. He has been accepted for graduate study at Vanderbilt University beginning in the fall of 1976.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Cp - Cyclopentadienyl

CPPh - Triphenylphosphoniumcyclopentadienylide

DMSC - Dimethylsulfoniumcyclopentadienylide

DMSO - Dimethylsulfoxide

DPE - 1,2-Diphenylethane

IR - Infra-red

MO - Molecular Orbital

NMR - Nuclear Magnetic Resonance

THF - Tetrahydrofuran

TMSC - Trimethylsilylcyclopentadiene

SOME NEW METALLOCENES

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The synthesis and characterization of some new metallocenes is discussed. These organometallic compounds contain some of the first reported pi-complexes between an aromatic ylid, triphenylphosphoniumcyclopentadienylide, and some transition metals.

Also reported is the synthesis of some new mercury halide metallocenes involving dimethylsulfoniumcyclopentadienylide as the sigma bonded organic substrate.

I INTRODUCTION

SOME NEW METALLOCENES

CYCLOPENTADIENYL-TRANSITION METAL COMPLEXES

The first metallocene was discovered accidentally by two independent groups. Bis(pentahaptocyclopentadienyl)iron(II) was first prepared by the reaction of iron(III)chloride and cyclopentadienyl magnesium bromide[1] and independently by the reaction of reduced iron, in the presence of K_2O, with cyclopentane in nitrogen at 300°C.[2] The product is an orange solid melting at 173°C and is sublimable. It is soluble in organic solvents such as alcohol, ether and benzene, however it is insoluble in water, 10% NaOH or concentrated HCl. It can be easily oxidized to a cation that is blue in solution. The cyclopentadienyl rings, being aromatic in character, undergo many of the same reactions as benzene. It is the most stable of the metallocenes and is known to the world by its trivial name 'ferrocene'.

The cyclopentadienyl grignard reagent or cyclopentadienide salts of alkali metals are widely used in the synthesis of other metallocenes. The most common general method used in the preparation of metallocenes is the addition of an anhydrous metal halide to a solution of sodium cyclopentadienide in tetrahydrofuran or polyethers. Iron will react directly with

cyclopentadiene, however high temperatures are required, while amines can be used to remove the acidic hydrogen of cyclopentadiene and thus allow the formation of the 'sandwich' complex at lower temperatures.[3] Cyclopentadienyl compounds have now been prepared for many of the transition metals in a variety of oxidation states.

X-ray analysis along with a host of other chemical and physical analyses have shown ferrocene to have a 'sandwich' structure. The structure of the molecule along with its thermal stability (over 500°C) have inspired a large amount of research work on this compound and the sizable group of related compounds. With respect to structure there are two main categories into which the non-ionic metallocenes can be placed. In one category are compounds which have a single metal-carbon sigma bond (monohapto), and in the other category are those which have one or more $(h^5\text{-Cp})M$ groups (pentahapto).

Neutral metallocenes have been obtained for all the 3d elements and all appear to have the same basic structure and bonding as ferrocene with the exception of magnesium and titanium. Only ferrocene is air stable, the others being susceptible to air oxidation; the stability order is Ni>Co>V>Cr. And doubts have been cast as to the actual existence of the $(h^5\text{-Cp})_2Ti$.[5]

The basic qualitative features of bonding in ferrocene and related structures are considered fairly well understood; however much research is continuing to refine the structure.[4] Before taking up a discussion of the bonding it should be noted

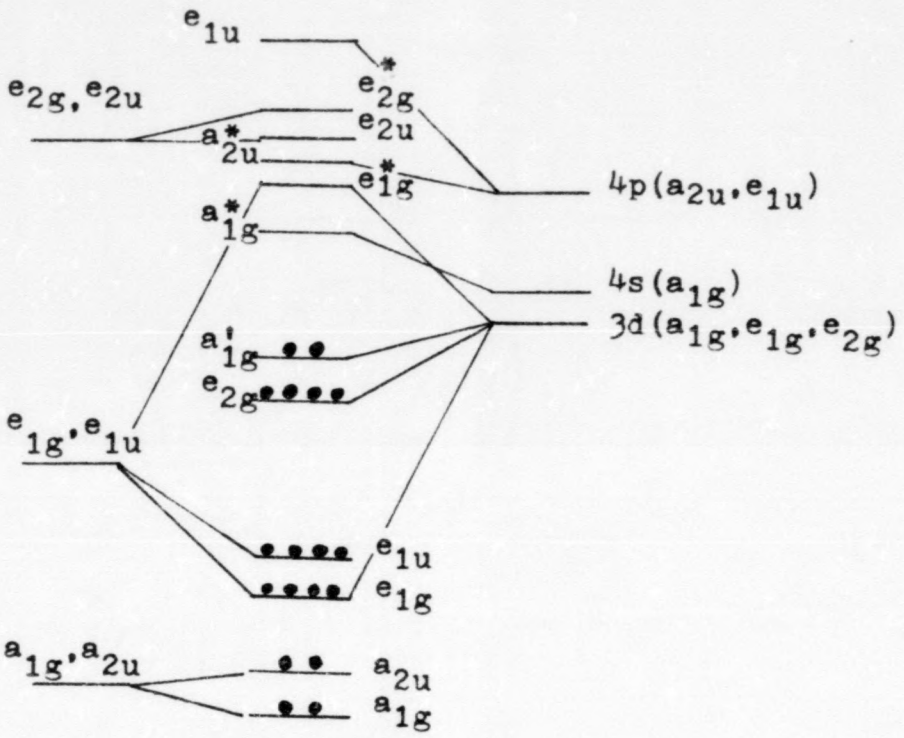
that the rotational orientation of the rings is not a critical topic nor is it one that has been absolutely settled. What is certain, however, is that the barrier to rotation between the staggered and eclipsed configuration is certainly low (less than 5 kJ mol^{-1}), and most of the recent studies indicate that in the crystalline state the eclipsed configuration may be the more stable.[6]

A semiquantitative energy-level diagram is given in Figure 1. Each cyclopentadienyl ring is considered as a regular pentagon with five pi MO's, one strongly bonding (a), one degenerate pair which is weakly bonding (e_1) and another degenerate pair which is strongly anti-bonding (e_2). Thus the pair of rings taken together has ten pi orbitals with symmetry such as to have centro-symmetric (g) and anti-symmetric (u) combinations.

For ferrocene there are 18 valence electrons, five from each ring and eight valence shell electrons from the iron atom. Thus the 18 electrons just fill the bonding and non-bonding MO's giving a closed configuration.

The mono-hapto (sigma bonded) cyclopentadienyl-transition metal compounds are the other class of non-ionic metallocenes. The fluxional nature of these compounds is considered to be common[7]. NMR studies indicate rapid rearrangement at higher temperatures by the appearance of one single sharp peak arising from the five protons on the ring. This line broadens into a complex spectral pattern at lower temperatures.

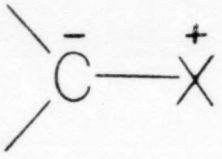
Figure 1


e_{1u}
e^*_{2g}
e_{2g}, e_{2u}
e_{2u}
a^*_{2u}
e^*_{1g}
$4p(a_{2u}, e_{1u})$
a^*_{1g}
$4s(a_{1g})$
$3d(a_{1g}, e_{1g}, e_{2g})$
a'_{1g}
e_{2g}
e_{1g}, e_{1u}
e_{1u}
e_{1g}
a_{1g}, a_{2u}
a_{2u}
a_{1g}
Cp
$(Cp)_2Fe$
Fe

It is the temperature lowering which effects a fairly rigid sterochemistry and thus slows down the hydrogen exchange rate. Detailed studies[8,9] have shown the rearrangement pathway to be a sequence of 1,2 metal shifts with such shifts having energies of activation[9] in the range 30-40kJ mol.$^{-1}$ for the $(h^5\text{-Cp})M(CO)_2(h^1\text{-Cp})$ (M = Fe or Ru) compounds.

YLIDES AND THEIR TRANSITION METAL CHEMISTRY

"An ylid can be defined as a substance in which a carbanion is attached directly to a heteroatom carrying a high degree of positive charge--represented by the general formula given below."[10]



It is the stabilization of the carbanion by the adjacent heteroatom which gives them their unique place in organic chemistry. It is this stability which allows them to be isolated as crystalline, stable substances whereas normal carbanions are seldom isolable.

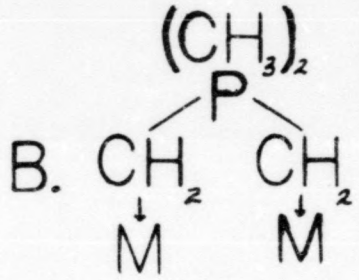
The field of transition metal-ylid chemistry is receiving great attention at present and as result there seems to be arising from the large variety of types of products a general classification scheme whereby they may be classified. The ylides may occur as simple terminal ligands (A), as bridging groups (B), or as chelating moieties (C), and all involving sigma bonding.[11]

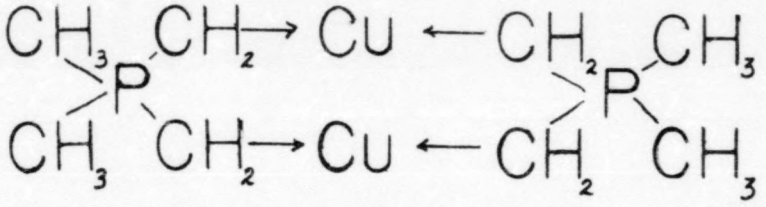
Figure 2

Ylid-Transition Metal Bonding Types

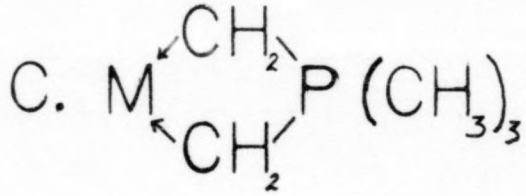
A. $R_3P\text{-}CH_2\rightarrow M$ $\quad [(CH_3)P\text{-}CH_2\rightarrow Cu\leftarrow CH_2\text{-}P(CH_3)_3]^+$

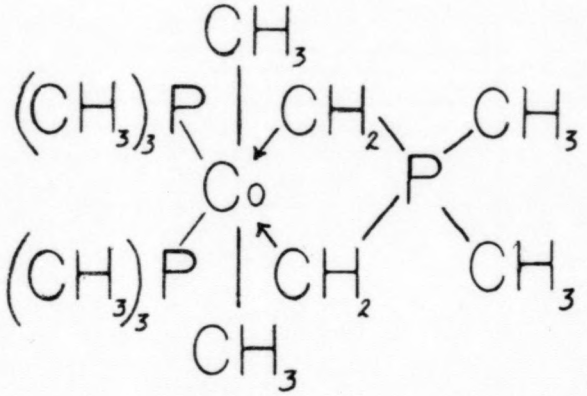
B.





C.





One of the properties associated with transition metal-ylid complexes is their unusual thermal stability. This is not unexpected for the complexes of the d^{10} metal ions of zinc, cadmium, and mercury because these metals furnish organometallic compounds that are generally stable anyway. Generally, products of d^{10} metals are of the B-type structure. Copper forms complexes in which the Cu-C sigma bond is stable well above room temperature. Silver also forms compounds of interest since their ^{1}H and ^{31}P nmr spectrum can be analyzed and the ^{1}H-C-$^{107,109}Ag$ couplings can be observed directly thus providing direct evidence for the Ag-C bond. Gold exhibits an even wider range of stable ylid compounds and with this element the 3+ oxidation state is found in a square planar d^{8} configuration.[11]

Stable compounds of well established structure are known for divalent and zerovalent nickel, salt-like structures for palladium and platinium and interesting structures of chromium, cobalt, iron, manganese and vanadium and their homologs.[11] An excellent article covering the area of the inorganic chemistry of ylides has been published by Schmidbaur.[11]

With the exception of the carbonyls of tungsten, chromium and molydenum,[12] pi complexes between ylids and transition metals are unknown. The chemistry of this area is the chemistry of the sigma bond. With this fact in mind we have attempted to utilize the aromatic character of two well characterized cyclic ylids in an attempt to synthesize systems analogous to the metallocenes already discussed.

CHARACTERIZATION OF CPPh AND DMSC

In this study we have used two ylids that are very analogous to the cyclopentadienyl (Cp) ligand associated with metallocenes. The two ylids, triphenylphosphoniumcyclopentadienylide (CPPh, Figure 3), and dimethylsulfoniumcyclopentadienylide (DMSC, Figure 4), have been the subject of considerable investigation with respect to their structure and their organic chemistry.[13,14]

CPPh was first prepared by Ramirez and Levy[15] in 1956. The molecule is constructed of a cyclopentadienyl ring containing a exocyclic triphenylphosphonium group. It is best exemplified by its carbon analog fulvene. Ramirez first pointed out the aromatic character of CPPh by the fact that diazo coupling took place on the cyclopentadienyl ring.[16] Later Yoshida verified the aromaticity of the ring by various reactions with dienophiles and electrophiles.[13,17]

DMSC was first synthesized by Behringer[18] in 1965. However, until 1971 no reactions using it had been reported except diazo coupling.[18] In 1971 Yoshida began his studies of the reactions and electronic structure of both CPPh and DMSC.[13,14,17,19,20]

As shown in figures 3 and 4 the ground state structures of the two ylides can be represented by both dipolar ylid and covalent ylene structures. Ramirez described the contribution of both forms as being equal based upon the observed pi-dipole moment (7D) which corresponded to the average

of the calculated pi-moments of the ylid and ylene forms (0.0D for 3c and 14.0d for 3a).[15] Yoshida, in an attempt to take into account the contribution from the sigma moment, utilized a semiempirical MO method ("molecules in molecule method") in combination with the electronic spectra of CPPh and DMSC to determine the correct contributions of each dipole moment. He found that the ground state aromatic character has 88% ylid and 12% ylene structure. This means that the five membered ring has appreciable aromatic character.

Both compounds exhibit an AA'BB' type of multiplet in the nmr spectrum for the five membered ring protons. For DMSC this multiplet is centered at tau 3.8(4H), while that of CPPh is located at tau 3.7(4H). The methyl H's of DMSC are found at tau 7.4(6H), while the phenyl H's of CPPh are seen as two multiplets centered at tau 2.2-2.6(15H).[13,14]

The UV data for CPPh and DMSC are found listed in table one.

Yoshida continued his study of the ylide-ylene nature of the carbanion-heteroatom bond by investigating the reactions of DMSC and CPPh with both dienophiles and electrophiles in order to further elucidate the nature of both the ylide-ylene bond and the extent of the aromatic character of the ring. He found no evidence for the Diels-Alder products which would be expected if the ylene form was significant. What he did find was that the reactions of the dienophiles and electrophiles

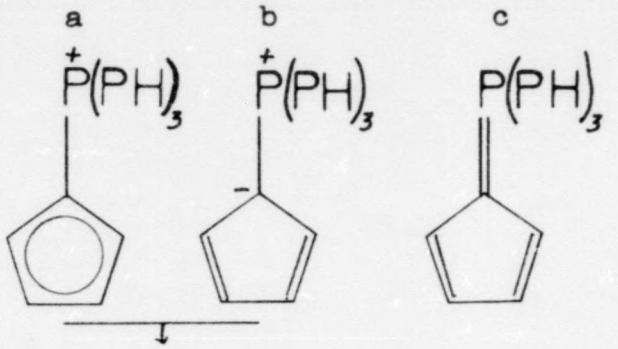


Figure 3

Ylid Structure Ylene Structure

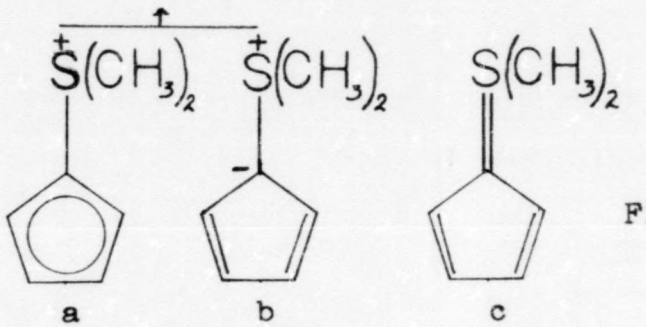


Figure 4

Table 1 Ultra-violet Absorption Data

	CPPh (CH_3CN)	DMSC (CH_2Cl_2)
λ_{max}	220mμ, 250mμ, 295mμ	283mμ
ϵ	3.82×10^4, 2.16×10^4, 5900	1.15×10^4

strongly supported the 5C 6-pi aromatic character of the aromatic character of the cyclopentadienyl ring in both ylides. Both compounds demonstrated the formation of exclusively 2-substituted derivatives. It was this uniqueness of reaction site that prompted the subsequent investigation of the reactivity of CPPh in terms of the ionization potentials as calculated by Huckel MO theory and the reaction position predicted from electron transfer theory, superdelocalizabilities, and localization energies.

The pi-electron densities (q_r) and pi-bond orders were found to be as shown in Figure 5 and Table 2. As anticipated the highest density was at C-1, however any reactions would be expected to occur at the three or four position assuming steric factors effecting substitution at position one. This is obviously in disagreement with the experimental evidence since all reactions occur at C-2. However these indices are for the molecule in an unperturbed state and there is no accounting of energy differences between ground and transition states. The more reliable indices, superdelocalizabilities (S_e), the localization energies (L_r), and the free valences (F_r) of the intermediate in electron transfer theory were evaluated and are listed in Table 2. As can be seen from the table those indices which do not involve pi-electron density show that electrophilic attack at the two position is the one expected.[13]

Yoshida also felt, after considering all the reactions of DMSC and CPPh, that DMSC is likely to be more reactive than

CPPh because of the milder conditions required for the DMSC reactions.

Thus it can be said that these two ylids have an aromatic character with respect to their 5-membered rings and the predominate resonance structure is the delocalized pi-electron ylid structure.[14]

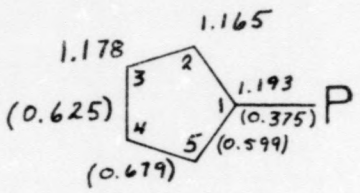


Figure 5
Pi-electron Densities and Pi-bond Orders

Table 2 Reaction Indicies for CPPh

	q_r	S_e	F_r	L_r	Bond Order
P	0.123	0.152			
					0.375
C_1	1.193	1.297	0.159	2.215	
					0.599
C_2	1.165	1.431	0.678	2.016	
					0.679
C_3	1.178	1.377	0.513	2.062	
					0.625
C_4	1.178	1.377	0.513	2.062	
C_5	1.165	1.431	0.678	2.016	

II RESULTS AND DISCUSSION

(DMSC)HgX_2 COMPLEXES

Our initial investigation began crudely with a series of test tube reactions utilizing common salts of some of the first row transition metals and DMSC. These reactions were performed without any special attention paid to the nature of the solvent conditions or possible action by the anion of the metal salt. They were merely to demonstrate that a new compound could be generated by the combination of these reactants. The instantaneous formation of seemingly new compounds was encouraging and we proceeded to determine the most favorable conditions to obtain these hopefully new metallocenes.

The first few attempts were made without regard to the extent of water and oxygen present in the solvents and atmosphere. Oxidizing anions such as nitrates and perchlorates were also used which further complicated the nature of the side reactions and gave non-productive results. While the formation of products was instantaneous, the melting points and elemental analyses indicated either that decomposition was occurring or that a variety of compounds were forming. Products have been obtained for all metals we attempted (see table 3) with the exception of Fe, Co, Pd, Ni. Attempts at purification, with the exception of the mercury compounds, proved futile owing to the poor solubility of the products

in most solvents or competition between ylid and solvent for coordination sites on the metal. Details concerning the melting points, and reaction conditions can be found in the experimental section.

It was not until we turned to the metal halides and more scrupulous reaction conditions with regard to oxygen and water-free solvents and atmospheres that productive results began to develop.

The mercury halides gave good elemental analyses and spectral data with which to work. A list of the analyses can be found in Table 4.

The synthesis of biscyclopentadienyl-mercury(II) was reported by G. Wilkinson and T.S. Piper[21] in 1956. They proposed at that time a localized metal-carbon sigma bond based unon mercury's lack of suitable d orbitals for 'sandwich' bonding and the remoteness of ionic bonding possibilities. Furthermore by comparisons of ultraviolet and infrared spectra of the $(Cp)_2Hg$ compound to known sandwich compounds it was felt that the complex contained a monohaptocyclopentadienyl ring. The type of bonding involved in this compound has been the subject of several papers.[22]

F.A. Cotton and T.J. Marks[22b] utilized a reference compound of known pentahaptocyclopentadienyl configuration, specifically $(h^5\text{-Cp})Ni(NO)$. As a reference standard for the monohaptocyclopentadienyl system, $(CH_3)_3Ge(Cp)$ was used.

The infrared spectrum for C_5H_6 is a simple one, consisting of a medium band at 3050-3100cm^{-1}, a strong band at 1000cm^{-1} and a broad very strong band at 800$\pm$ 50cm^{-1}, with possibly two more weak bands at 1400cm^{-1} and 1100cm^{-1}. For a (h^1-Cp)M system there is much more complexity arising from the 24 normal modes of vibration from the ring itself. Indeed a look at the spectrum of the monohapto compounds, even with the $Ge(CH_3)_3$ portion eliminated, shows a complex spectrum quite unlike that expected for the more symmetrical pentahapto complex. It was the conclusion of Cotton and Marks, based upon this comparison, that the complex was a monohaptocyclopentadienyl complex.

Maslowsky and Nakamoto[22d] undertook a study of the bonding much along the same lines as Cotton and Marks. They also utilized IR spectra comparisons between known reference standards and various mercury-cyclopentadienyl halide complexes, and extended the bonding type possibilities to include a trihaptocyclopentadienyl type complex, using as the standard $(Cp)_2Mo(NO)I$. They too eliminated the pi-sandwich and pi-allylic structure and chose the sigma bonded structure as the one of preference (see Table 5 for a list of IR vibrational frequencies and their assignments). This group attempted a PMR study of the complexes but observed no change in the spectra despite both temperature and solvent changes. This is contrary to what would be expected if one could 'freeze' the molecule so as to obtain a non-fluxional configuration

and thus create a non-uniform magnetic effect on the ring hydrogen's. The fluxional behavior is observed because the means exist whereby the mercury atom has an equal probability of being attached to each of the five carbon atoms of the cyclopentadienyl ring.

West, Woodville and Rausch[22c] performed NMR studies on the CpHgCl molecule in THF-d^6 in a temperature range of 22°C to -113°C and found the spectra to be consistent with a fluxional molecule with a nuclear configuration of:

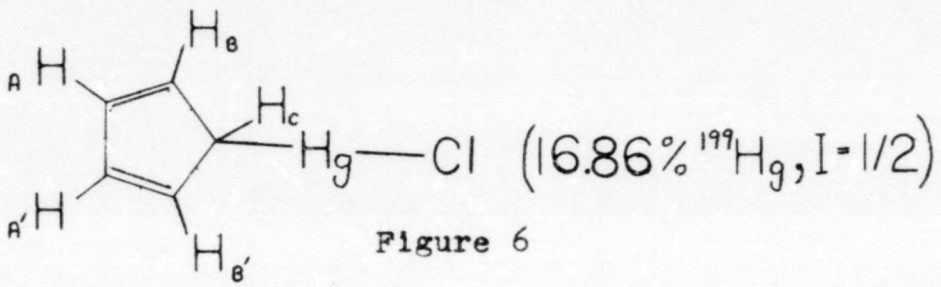


Figure 6

At -113°C the interconversion between nuclear configuration is slow enough to reveal the instantaneous structure in its NMR spectrum. The observed spectrum at -113°C is a superposition of three magnetically equivalent molecules, 83.14% CpHgCl (AA'BB'C), 8.43% Cp^{199}Hg(alpha)Cl (AA'BB'CM) and 8.43% Cp^{199}Hg(beta)Cl (AA'BB'CM) which would be consistent with the above figure.

It should be pointed out that the logical tool for determining the structure of $(Cp)_2Hg$ would be X-ray diffraction. However, the difficulty in growing single crystals of Hg complexes and their decomposition upon exposure to light preclude this useful structural tool.

Product formation, indicated by immediate precipitation, has been instaneous in all of our Hg reactions with DMSC except for the iodide complex, which required petroleum ether to effect precipitation. The chloride and bromide products are tan and the iodide is yellow. All the complexes have been soluble in DMSO with no apparent product degradation indicated by the NMR spectra even after 24 hours. Thus it may be possible to grow crystals opening a possible route for purification as well as spectral characterization.

We will attempt to utilize comparisons of IR spectra in order to demonstrate the bonding present in these ylid-mercury complexes. In Table 6 are listed all observed bands of some $(CPPH)HgX_2$ complexes which are known to have Hg-Carbon sigma bonds at the three position of the Cp ring,[22e] but still postulated to be fluxional molecules. By analogy we would expect the spectra of the $(CPPH)HgX_2$ to be more complex than the original ylid. As can be seen this is the case with the appearance of a much more complex spectrum. New bands appear in the region 790-935cm^{-1}, 1085cm^{-1}, 515cm^{-1}. NMR spectra also indicate the retention of the aromatic character of the cyclopentadienyl ring showing essentially single broad single peaks at 6.25 delta for the bromide, 6.35 delta for the chloride and a multiplet for the iodide centered at 6.46 delta.

A comparison of the $(DMSC)HgX_2$ IR spectra with the DMSC ylid shows a lack of increased complexity as would be expected from the analogous $(CPPH)HgX_2$ complexes compared

to their respective ylids. The IR spectra of the chloride species does show, however, a new broad band at 870cm^{-1} and 815cm^{-1} with the rest of the spectra being essentially identical to the ylid spectrum, most of the bands being shifted to higher frequency (see Table 7). The bromide's spectrum, taken as a Nujol mull, is heavily blocked by the dispersion medium, but we do see here also the appearance of a strong band at 840cm^{-1} and 790cm^{-1} and a loss of intensity of the band at 1130cm^{-1} which corresponds to 1165cm^{-1} in the ylid spectrum. The iodide shows the greatest deviation from the ylid of the three, once again the new bands at 840cm^{-1} and 800cm^{-1} but also increased intensity of the 590cm^{-1} band. Despite these minor changes the mercury halide complexes retain the essential structural simplicity of the ylid.

In the NMR spectra of the (DMSC)HgX_2 complexes (Table 8) while we still see retention of the rings aromatic character we also see down-field shifts of both the Cp ring and the methyl hydrogen's, and also the separation of the original AA'BB' type pattern to a pattern more closely resembling a AA'MM' type multiplet. This pattern would indicate either monohaptocyclopentadienyl type attachment at the one position of the ring or possibly a trihaptocyclopentadienyl type bonding over the C_1-C_3 of the ring. We favor the monohapto structure which would be consistent with the past Hg-Cp complex bonding and also that of the ylid-transition metal chemistry. The trihapto type of structure, would be expected

to yield an up-field shift by the C_3,C_4 hydrogen's which is not what we see, however, this structural possibility cannot be entirely eliminated without further evidence.

(CPPH)$TiCl_x$ COMPLEXES

Derivatives containing pi-cyclopentadienyl ligands make up most of the organometallic chemistry of titanium. The most important of these are (1) biscyclopentadienyl titanium dichloride, $(Cp)_2TiCl_2$, utilized in Ziegler catalysis[23], (2) pi-cyclopentadienyl derivatives of titanium(III) and (3) titanocene, $(Cp)_2Ti$, which has been extensively studied with respect to both its structure and its nitrogen fixation properties[24].

The $(Cp)_2TiCl_2$ compound has what can be considered an 'angular' sandwich structure having a dipole moment of 6.3D thus indicating that the structure approaches a tetrahedral configuration[25d]. The red, air-stable crystals melt at 289-291^{o}C and are insoluble in water and to varying degrees are soluble in organic solvents.

The proton magnetic spectrum exhibits a sharp singlet at 6.5-7.0 delta in THF and the infrared spectrum exhibits the normal vibrations in the region 650-4000cm^{-1} of a pi-bonded cyclopentadienyl ligand, 3100cm^{-1} (CH stretch), 1435cm^{-1} (CC stretch), 1020cm^{-1} (CH deformation in-plane) and 820cm^{-1} (CH deformation out-of-plane). These four bands are consistent in the series Ti, Zr, and Hf with the 800cm^{-1} band shifting to lower range with a decrease in the oxidation state of the

metal.

The normal method of preparation being a reaction between $TiCl_4$ and either the Grignard reagent, CpMgBr, or the sodium, lithium, or magnesium salts of cyclopentadienide.

The usual preparation of the Ti(III) cyclopentadienyl derivatives is by the reduction of $(Cp)_2TiCl_2$ using a reducing agent such as Zn, to form $((Cp)_2TiCl)_2$ and $ZnCl_2$ or by using two moles of NaCp added to the Ti(IV) species to produce $(Cp)_3Ti$ and NaCl, however the addition of $TiCl_3$ to NaCp can also be used. The resulting complex, a green-brown solid, can be purified by sublimation at 170°C in a vacuum, is soluble in air-free water and most organic solvents and melts at 282-283°C[25a].

Titanocene, $(CP)_2Ti$, has been the center of considerable investigation with respect to its structure.[26b] It was first prepared in 1956 by Fisher and Wilkinson by the reaction of $TiCl_2$ and NaCp in THF and later modified by Watt, Baye and Drummond[26b] using the $(Cp)_2TiCl_2$ complex reduced to Ti(II) by the action of a THF solution containing sodium and napthalene. The titanocene as prepared by Watt, et.al. was sublimed at 100°C. The infrared spectrum suggests that the cyclopentadienyl groups are not symetrically pi-bonded, and no bands ($2000cm^{-1}$) are found attributable to a Ti-H stretch despite the fact that these are found in several other isomers. This titanocene is diamagnetic and in d^8-toluene shows PMR spectral bands between 5.19 delta and 6.79 delta

at 30°C and move downfield to between 5.66 delta and 7.56 delta at 90°C. It is soluble in THF, thermally stable up to 200°C, but reacts with water, oxygen, halogenated solvents, carbon disulfide, sulfur dioxide, dimethyl sulfide and nitromethane and has been shown to fix nitrogen.[27]

We have prepared CPPh derivatives of titanium in the two, three, and four oxidation states. However attempts at characterization have been frustrated by our inability to find suitable solvents for NMR analysis and the sensitivity exhibited by all of these compounds to oxygen and water have inhibited our ability to obtain suitable IR spectra.

The Ti(IV) species exhibit a wide range of colors from tan to deep violet depending apparently upon reaction conditions. This complex seems to absorb water rapidly, as two consecutive IR scans indicate a high rate of water absorption from the atmosphere (increasing intensity of the broad band from 3500-2800cm^{-1}). This occurred despite the KBr pellet being formed in an argon atmosphere. The physical characteristics of the Ti(III) and Ti(II) are taken up individually in the experimental section.

A comparison of the IR bands appearing in both the ylid and the three derivatives of titanium-CPPh (see Table 9) show the three complexes as having retained the spectral characteristics of the ylid ligand showing shifts to longer wavelengths. The Ti(IV) species shows a new strong band in the 1510-1615cm^{-1} area, and a broadening and flattening of the

band in the 280-530cm^{-1} region. The Ti(III) species is almost identical to the ylid ligand spectrum with the exception of the disappearance of the band at 1140-1190cm^{-1} and a broadening and intensification of the band centered at 2995cm^{-1}. In the Ti(II) species we see once again the appearance of no new bands but a loss of the bands at 1140-1190cm^{-1} and an increase in the intensity of the band centered at 2995cm^{-1}. This lack of increased complexity in the spectra coupled with the elemental analyses leads us to believe the bonding to be pi-type with respect to the cyclopentadienyl ring as is observed in the titanium-cyclopentadienyl derivatives and the ylid-transition metal carbonyl complexes of Wilkinson[12].

$(CPPh)_2WCl_6$ COMPLEX

The bispentahaptocyclopentadienyl derivatives of tungsten have not as yet been reported however the dihydrides $(Cp)_2WH_2$ have been prepared by the action of WCl_6 and NaCp. This low yield method can be improved through the addition of $NaBH_4$ as a hydrogen source.[25c] The resulting yellow, volatile air sensitive solids can then be converted into the dihalide complexes by their reaction with halogenated solvents, stronger halogenating agents tending to oxidize the dihalides to cations of the form $(Cp)_2WX_2$, often obtained as HX_2^- salts.

The dihalides are all dark green crystals which are soluble in liquid SO_2 from which they can be recrystallized. They are stable to oxidation for several weeks, are diamagnetic, nonvolatile and decompose at about 250°C without melting. They can be considered essentially analogous to the bispentahaptocyclopentadienyl halides of titanium, all of which have a tetrahedral configuration.

The $(CPPh)_2WCl_6$ complex precipitated as a grayish-green powder melting in the range 175-177°C. We were unable to recrystallize the product owing to a lack of suitable solvents. An IR spectrum was obtained in KBr and is listed in Table 10 along with the NMR data taken using DMSO as a solvent. Once again we see no new complexity developing in the IR spectrum relative to the ylid ligand. New bands do appear at 275cm^{-1} and 290cm^{-1}, and bands associated with the ylid at 1140cm^{-1}, 1160cm^{-1}, 1180cm^{-1} and 1190cm^{-1} are not seen in the tungsten spectrum. The NMR spectrum reveals that the cyclopentadienyl ring remains aromatic but is shifted far downfield to approximately 8.2 delta placing it below the the phenyl absorption at 7.6 delta. The lack of complexity of the infrared spectrum, coupled with the aromatic character of the ring offers evidence for the pi-type bonding scheme.

$(CPPh)_2IrCl_3$ COMPLEX

The bispentahaptocyclopentadienyl cation of Ir(III) can be obtainted by the reaction of the anhydrous trichloride with cyclopentadienyl magnesium bromide under vigorous

conditions and is isolated as the hexafluorophosphate.[25b] The neutral monomeric derivatives analogous to cobaltocene have not been isolated, this owing apparently to the unstable nineteen electron configuration. However the yellow dimer, $(Cp)_4Ir_2$ has been obtained by treating the phosphate salt with molten sodium. The $(Ir(Cp)_2)PF_6$ exhibits the following IR bands 3145,2941,1412,1110,1062,1012,994,916,876,869,838, 827,818,776,560,392cm^{-1} and exhibits a PMR signal at 6.04 delta in acetone. The product we obtained was a dark brown precipitate which did not melt below 300°C. It gave an unsatisfactory elemental analysis, however the IR spectrum is very similiar to the ylid with the exception of new bands at 295cm^{-1} and 325cm^{-1} probably due to Ir-Cl stretching, and also new bands at 1550,1580,1880 and 1890cm^{-1} with the bands at 3340cm^{-1} and 3020cm^{-1} becoming very broad.

III EXPERIMENTAL PROCEDURE

GENERAL TECHNIQUE

The following experimental procedures and conditions were adhered to in the syntheses of the transition metal-ylid complexes.

Most syntheses were carried out at room temperature and usually under an inert atmosphere of nitrogen or argon. The general procedure was to add dropwise a metal salt which had first been dissolved in a minimal amount of tetrahydrofuran (unless insolubility of the salt (FeI_2) or metal-solvent complexation (WCl_6) dictated direct addition of the salt) to a stirred solution of the ylid in THF. With the exception of the mercury complexes the ratio of ylid to metal salt was 2:1, the ratio being 1:1 for the mercury halides.

In almost all cases there was an immediate precipitate formation and the mixture was allowed to stir for approximately thirty minutes before collecting the product under an inert atmosphere. The addition of dry petroleum ether was used where necessary to aid precipitation.

All glassware was pre-dried and only fritted glass funnels were used for filtration. All solvents were dried and freshly distilled prior to each synthesis to avoid contamination by oxygen and water. THF was dried using a sodium/benzophenone mixture and distilled under an inert

atmosphere, usually nitrogen. Because titanium complexes are known to fix nitrogen, argon was employed for these complexes. Petroleum ether was dried using calcium hydride. The hexahydrate of nickel perchlorate was treated with dimethoxypropane to remove the water of hydration.

TRIPHENYLPHOSPHONIUMCYCLOPENTADIENYLIDE (CPPh)

CPPh was prepared by the method of Ramirez[15] and had a mp of 235-236°C (lit. 229-231°C). CPPh was also obtained commercially, however further recrystallization was performed using a fifty percent chloroform and ethanol mixture.

DIMETHYLSULFONIUMCYCLOPENTADIENYLIDE (DMSC)[29]

To a stirred solution of 30g.(0.45mole) of cyclopentadiene in 300ml of THF was added, under nitrogen, 270ml(0.648mole) of n-butyl lithium within a half-hour and the mixture was stirred for an additional half-hour. To this solution was added dropwise 74g(0.68mole) of chlorotrimethylsilane. The resultant thick slurry was stirred for a half-hour and then filtered to remove the white salts. The THF was removed from the filtrate by first distilling at atmospheric pressure using a Widmer column and then distilling the silane derivative under vacuum at 40-45°C and 30-35mm^2(lit. 43-44/19mm^2) to obtain the trimethylsilylcyclopentadiene (TMSC).

To a stirred solution of 20ml of the TMSC in 30ml of petroleum ether was added 20ml of dimethylsulfoxide (DMSO) and the mixture was stirred for 24 hours at room temperature. The solution became discolored and formed two layers. The

layers were separated and the lower brown-colored layer was treated with ether to separate a tan crystalline product which gave a mp 139°C (lit. 134°C) after recrystallization from benzene and petroleum ether. This material corresponded in mp, NMR, and IR with those reported for the ylid.

$(CPPh)_5Ti(II)Cl_2$ SYNTHESIS

The method, with a slight modification, was analogous to that employed by G.W.Watt.[26b] In a dry, argon atmosphere 0.05g(2mmoles) of sodium was added to a stirred solution of 0.336g(3mmoles) of napthalene in 25ml THF. The solution became a dark green with the appearance of the sodium napthalide. The mixture was allowed to stir until all traces of metallic sodium had disappeared. The napthalide was allowed to form prior to the addition of the titanium(IV) complex because there was no reaction unless the napthalide was preformed. To the stirred sodium napthalide solution was added 0.289g (.34mmoles) of $(CPPh)_2Ti(IV)Cl_4$, with the reaction considered complete with the discharge of the napthalide's green color. A sample of the resultant yellow precipitate decomposed immediately upon contact with the atmosphere. There was substantial darkening of a sample after 24 hours even though it was stored under argon and at -20°C.

1,2-DIPHENYLETHANE (DPE)

Alpha-chlorotoluene was added to the THF/napthalene/NaCl/ $(CPPh)_2Ti(II)Cl_2$ mixture in an attempt at dimerization to DPE.

The mixture was allowed to set for one hour then a thin-layer chromatographic analysis was performed on the liquid. No DPE was isolated indicating no dimerization had occurred.

NITROGEN FIXATION

A portion of the reaction mixture of $(CPPh)_2Ti(II)Cl_2$ was put under a nitrogen atmosphere for 24 hours in an attempt at possible nitrogen fixation, however no ammonia formation was indicated using a wet litmus paper test.

$(CPPh)_2Ti(III)Cl_3$ SYNTHESIS

To a stirred solution of 1.0g(3.06mmoles) of CPPh in 100ml of THF at room temperature was added, under argon, 0.24g(1.56mmoles) titanium(III)chloride. The solution was allowed to stir for 24 hours and a resulting cream colored precipitate (0.74g) was collected which gave a wide melting point (with decomposition) range (approximately 80-220°C).

INSTRUMENTATION

All infrared and nuclear magnetic resonance spectra were taken from a Perkin-Elmer 457 grating infrared spectrophotometer and a Varian A-60A NMR spectrometer, respectively. A Fisher-Johns melting point apparatus was used for all melting point determinations.

Table 3 Reaction Conditions and Results

COMPLEX	METAL(mmoles)	YLID(mmoles)	SOLVENT
$(CPPh)_2Ni(ClO_4)_2$	$Ni(ClO_4)\cdot 6H_2O$ 1.76mmoles	CPPh 3.7mmoles	$CHCl_3$(wet)
$(CPPh)_2Pd(NO_3)_2$	$Pd(NO_3)_2\cdot 2H_2O$ 0.25mmoles	CPPh 0.75mmoles	ACETONE(wet)
$(CPPh)_2Ni(ClO_4)_2$	$Ni(ClO_4)\cdot 6H_2O$ 0.62mmoles	CPPh 3.10mmoles	20ml $CHCl_3$ 20ml ACETONE
$(CPPh)_2Co(NO_3)_2$	$Co(NO_3)_2$ 0.64mmoles	CPPh 3.0 mmoles	60ml THF
$(CPPh)_2FeI_2$	FeI_2 0.52mmoles	CPPh 1.0 mmoles	60ml THF
$(CPPh)_2WCl_6$	WCl6 0.95mmoles	CPPh 3.8 mmoles	75ml THF
$(CPPh)_2IrCl_3$	$IrCl_3\cdot 2H_2O$ 0.52mmoles	CPPh 0.996mmoles	40ml THF
$(CPPh)_2TiCl_4$	$TiCl_4$ 5.3mmoles	CPPh 18 mmoles	1200ml THF
$(DMSC)_2FeI_2$	FeI_2 3.96mmoles	DMSC 3.97mmoles	100ml THF
$(DMSC)HgCl_2$	$HgCl_2$ 3.96mmoles	DMSC 3.96mmoles	40ml THF
$(DMSC)HgBr_2$	$HgBr_2$ 3.96mmoles	DMSC 3.96mmoles	75ml THF
$(DMSC)HgI_2$	HgI_2 3.96mmoles	DMSC 3.96mmoles	55ml THF
$(DMSC)_2Ni(NO_3)_2$	$Ni(NO_3)_2\cdot 6H_2O$ 1.0mmoles	DMSC 1.5mmoles	ACETONE
$(DMSC)_2FeI_2$	FeI_2 3.96mmoles	DMSC 3.97mmoles	100ml THF

Table 3 Continued

COMPLEX	ATMOSPHERE	MELTING POINT	REMARKS/ YIELD
$(CPPh)_2Ni(ClO_4)_2$	AIR	180-253°C decomp.	Green ppt. H_2O present/ 74.9%
$(CPPh)_2Pd(NO_3)_2$	AIR	190-197°C	Brown ppt. H_2O present/ 43.5%
$(CPPh)_2Ni(ClO_4)_2$	AIR	180-253°C decomp.	H_2O elimintd. using dimeth oxypropane
$(CPPh)_2Co(NO_3)_2$	NITROGEN		BLACK OIL
$(CPPh)_2FeI_2$	ARGON		NO REACTION
$(CPPh)_2WCl_6$	ARGON	175-177°C	gray ppt./ 62.2%
$(CPPh)_2IrCl_3$	ARGON	NO MELTING POINT BELOW 300°C	Brown ppt. H_2O present/ 60.6%
$(CPPh)_2TiCl_4$	ARGON	135-136°C	Tan powder turns violet /23.7%
$(DMSC)_2FeI_2$	NITROGEN		NO REACTION
$(DMSC)HgCl_2$	NITROGEN	140-141°C	Tan powder/ 80.3%
$(DMSC)HgBr_2$	NITROGEN	143-144°C	Tan powder/ 81.2%
$(DMSC)HgI_2$	NITROGEN	111-112°C	Yellow ppt./ 78.3%
$(DMSC)_2Ni(NO_3)_2$	AIR	180-260°C decomp.	Green ppt. H_2O present
$(DMSC)_2FeI_2$	NITROGEN		NO REACTION

TABLE 4 ELEMENTAL ANALYSES (Calculated/Found)								
	%M	%C	%H	%P	%S	%Cl	%Br	%I
$(DMSC)HgCl_2$	50.43 50.28	21.14 21.04	2.53 2.60		8.06 7.96	17.83 17.67		
$(DMSC)HgBr_2$	41.22 41.05	17.28 17.58	2.07 2.15		6.59 6.54		32.84 32.64	
$(DMSC)HgI_2$	34.55 34.45	14.48 14.68	1.74 1.72		5.52 5.29			43.71 43.79
$(DMSC)_2Ni(ClO_4)_2$	9.07 6.70	27.22 13.81	3.26 2.65		10.38 4.94			
$(CPPh)_2Ni(ClO_4)_2$	8.01 .80							
$(CPPh)_2TiCl_4$	5.69 5.5±1	65.55 61±3	4.55 5±.5	7.36 6.5±5		16.84 17±1		
$(CPPh)_2TiCl_3$	8.68 8.37	50.00 49.86	4.93 5.06	5.61 8.37		19.26 18.98		
$(CPPh)_2WCl_6$	17.52 16.73	52.65 51.53	3.65 4.20	5.90 5.33		20.27 17.27		

Note: All Analyses were conducted by Galbraith Laboratories of Knoxville, Tennessee.

TABLE 5[22d]

Vibrational frequencies of $(Cp)_2Hg$, Cp[a] and CpHgX types of compounds

$(Cp)_2Hg$[b]	CpHgCl[c]	CpHgBr[c]	CpHgI[c]	Cp	Assign.[d,e]
3090s[i]	3105m	3105s	3110s	3105m	v(CH)
3088s	3090m	3090s	3075s	3091s	v(CH)
3076sh	3072s	3063s	3060sh	3075m	v(CH)
3040sh	3040w	3030sh	3040sh	3043m	v(CH)
2970w	2950w	2960w	2960w		v(CH)
	1830w	1825w	1821w		combin.
1808w	1810w	1810w	1808w		overtone
1630w		1634m	1635w		combin.
1530w	1543w[g]	1540w[g]	1540w[g]	1540w	v(C=C)
1427m	1464m[g]	1460m[g]	1457m[g]	1441w	d(CH)
1383m	1379m	1378m	1379m	1365vs	d(CH)
1296m	1290m	1289m	1293m	1292m	d(CH)+ ring def.
1234m	1228m	1224w	1230w	1239m	d(CH)+ ring def.
1109w	1108w	1110vw	1110vw	1106w	ring def.
1084m	1089m	1086m	1086m	1089m	d(CH)
1026m	1026m	1019m	1022m		d(CC(5)H)
988m	990m	989s	988s		d(CC(5)H)
957m	962m	958m	952m	959s	ring def.+ d(CH)
907vs	941s	938vs	925vs	925sh	d(CH)
885vs	902s	901s	898s	920s	ring def
	885w	887w			
822m	819m	818s	820s	805m	ring def.
748vs	756vs	753vs	750vs	700vw	pi(CH)
720w	720w	718w	718w		combin.
646s	653s	650s	613s	664vs	d(CH)
575w	565w	564w	566w	515w	ring def.
348s	359s	342s	336s		asym v(HG-C(5))
	316s				v(Hg-Cl)
		232s			v(Hg-Br)
200m	197m	220m	220m		d(CC(5)Hg)
			186s		v(Hg-I)
100w	108w	53w	51w		d(C(5)HgX)[h]

[a]Carbon tetrachloride as the solvent. [b]Carbon disulfide and chloroform as the solvents. [c]Carbon disulfide as the solvent. [d]The assignments between 4000 and 500cm^{-1} are those given for C_5H_6. [e]v,stretching; d,in-plane bending; pi,out-of-plane bending. [f]These bands hidden by solvent. [g]These values are taken from the perfluorocarbon spectrum of the compound. [h]X = C,Cl,Br, or I. [i]Intensity designations: vs,very strong; s,strong; m,medium; w,weak; vw,very weak.

TABLE 6

Vibrational frequencies of $(CPPh)HgX_2$ types of compounds

$(CPPh)HgBr_2$	$(CPPh)HgCl_2$	$(CPPh)HgI_2$	CPPh
---	---	3000m	2995m
---	1558w	1560w	---
1450w	1458sh	1450sh	1450m
1410w	---	---	---
1390vs	1398vs	1380vs	1390s
1360s	---	---	---
1330s	1338w	1330m	1320m
1300m	1308w	1295m	1280sh
---	1268sh	---	---
---	---	1250sh	1250sh
---	1213w	---	---
1200w	---	---	---
---	---	1195sh	1190sh
---	---	---	1180sh
---	---	1170s	---
1160m	1163m	---	1160m
---	---	1150sh	1140sh
1090s	1093s	1085vs	---
---	---	1080s	1080s
1065s	1068s	---	1060m
---	---	1045sh	---
---	---	---	1030sh
1010w	1018w	1015sh	1010vs
980s	993vs	985vs	980sh
---	958sh	---	---
---	---	935s	---
---	893sh	895s	---
875w	878sh	875vs	---
835sh	843sh	835s	---
815s	823vs	810sh	---
790vs	808vs	790vs	---
740sh	748s	740s	740s
710s	718vs	710vs	700vs
680s	688vs	680vs	680vs
---	---	---	660sh
---	---	---	635sh
605m	608vs	600s	600m
540m	543vs	540s	535vs
515s	518s	515s	---
500s	503vs	500s	505s
---	---	---	490vs
---	448w	450m	---
---	---	435sh	---
---	---	---	420sh
---	---	405sh	---
NMR (delta units) Cp ring H's			
6.25	6.28	6.21	6.38
	6.48	6.72	6.58

TABLE 7

Vibrational frequencies of $(DMSC)HgX_2$ types of compounds

$(DMSC)HgBr_2$[a]	$(DMSC)HgCl_2$	$(DMSC)HgI_2$	DMSC
---	---	---	3010m
---	2960m	---	---
---	---	---	2940m
---	---	2930w	---
---	---	---	2870w
---	1480w	---	1475w
---	---	1455w	---
---	1410m	1405m	---
---	---	---	1380vs
---	1320w	1315w	1320sh
---	---	---	1300vs
---	---	---	1208w
---	---	---	1188sh
1130m	1140m	1155m	1165vs
---	---	---	1140sh
1055w	1060w	1060m	---
1025w	1030m	1030m	1030sh
1010w	1000w	1010m	1020sh
---	---	1005w	1005vs
980s	990s	985s	---
---	970m	---	---
955s	---	960m	965vs
---	---	920m	910w
---	870vs	870s	885w
840s	---	840s	---
---	---	---	830w
---	815s	800s	805m
790s	---	---	---
715m	725m	715m	710s
---	675w	675w	670m
---	640w	630m	630sh
---	595s	590s	580s
---	450s	450s	450s
---	350w	345s	345s
---	300w	---	310s
---	---	280m	275m
---	260w	255s	250w

[a]Spectrum taken as a nujol mull.

TABLE 8

NMR shift data, in delta units, for $(DMSC)HgX_2$ compounds.

$(DMSC)HgBr_2$	$(DMSC)HgCl_2$	$(DMSC)HgI_2$	DMSC
2.99(6H's)	3.08(6H's)	3.08(6H's)	2.9(6H's)
6.03 6.58 (4H's)	6.12 6.62 (4H's)	6.13 6.72 (4H's)	6.42 6.44 (4H's)

TABLE 9

Vibrational frequencies of $(CPPh)_2TiCl_x$ types of compounds

$(CPPh)_2TiCl_3$	$(CPPh)_2TiCl_4$	$(CPPh)_2TiCl_2$	CPPh
300m	280w	280w	280w
---	---	460w	450sh
490s	470m	500s	490vs
510s	500w	515s	505sh
535m	530m	550s	535vs
575w	600w	600w	600w
---	655w	665sh	635sh
680s	685s	685vs	680vs
715s	715s	710vs	700vs
745w	745s	740sh	740m
835s	795m	780sh	---
895sh	875s	870m	off scale
985s	985s	990s	off scale
1010s	1010w	1018m	980m
---	---	1025sh	1010s
1045w	1020vw	1040w	1030sh
1075sh	1070sh	1060sh	1060sh
1090s	1095vs	1090s	1080s
---	1130sh	1145vw	1140sh
---	---	1170vw	1160s
1195m	1170sh	1190vw	1180s
1230w	1245m	1200vw	1190sh
1295m	1295s	1325sh	1280m
1325m	1335s	1370sh	1320m
1410s	1415vs	1410vs	1390s
1445m	1460s	1455s	1450w
1545w	1530sh	1535sh	2640sh
2660w	1565vs	3020m	2995m
3060vs	1600vs	3330vs	
	1640sh		
	1660sh		
	1775m		
	1880w		
	1975w		
	3000vs		
	3330vs		

TABLE 10

Vibrational frequencies of $(CPPh)_2MCl_x$ types of compounds.

$(CPPh)_2WCl_2$	$(CPPh)_2IrCl_3$
275vs	295vs
290sh	325sh
500sh	490sh
515vs	510vs
545vs	530sh
680sh	540s
690vs	610w
700sh	650sh
720vs	665sh
750vs	675sh
810w	685vs
880w	690sh
910w	710vs
990m	745s
1100vs	795w
1180w	845w
1260vw	870w
1300w	905vw
1345w	985m
1410sh	1010sh
1420s	1055sh
1465m	1080sh
1970vw	1090vs
2800vw	1150w
3000m	1175w
3400vw	1250w
	1280vw
	1325m
	1360vw
	1400w
	1420m
	1460w
	1550w
	1580w
	1800vw
	1845vw
	1880w
	1890m
	2800-3400 vs

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